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SIGNIFICANT VAPOR PRESSURE CONSIDERATIONS OF THE VAN SLYKE MANOMETRIC METHOD OF GAS ANALYSIS

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ABSTRACT

The significance of vapor pressures in relation to the ***c correction*** of the Van Slyke manometric method of gas analysis is discussed. It is shown that the ***c correction*** changes with temperature in such a way that the determination of one such correction for a particular apparatus (and procedure) is inadequate. The prescribed Van Slyke technique may introduce errors amounting to several tenths of 1 percent in cases where the accuracy claimed is several hundredths of 1 percent. Other vapor-pressure considerations are discussed and possible errors pointed out. Two suggestions are offered to correct the difficulty, one of which involves a modification of the apparatus.

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INTRODUCTION

The development of satisfactory apparatus and methods for the analysis of the gases dissolved in blood has offered an unusually interesting problem. Among the investigations in this difficult and important field those of Van Slyke and his colleagues are outstanding. The manometric apparatus and methods of Van Slyke are extensively used for the analysis of dissolved gases; and these methods have been extended to include not only the analysis of many solutions by gasometric methods but also the macro- and micro-analysis of gas mixtures. A complete report of this work is given in "Quantitative Clinical Chemistry", vol. 2 (Methods), by John P. Peters and Donald D. Van Slyke (the Williams & Wilkins Co., Baltimore, Md., 1932). In the present discussion all references to details of the Van Slyke technique will be cited from this text.

Like all other methods of gas analysis, the Van Slyke manometric method is subject to a number of errors, most of them of small magnitude. And unlike some methods, that of Van Slyke is supplied with a number of painstaking procedures designed to eliminate

the inaccuracies caused by such errors. The purpose of this paper is to amplify one of the corrections prescribed and to point out that this correction is dependent upon temperature in such a manner that significant errors may sometimes occur when the correction is used as prescribed.

II. OUTLINE OF THE VAN SLYKE MANOMETRIC METHOD

A very brief résumé of the manometric method is presented for those who are not familar with the Van Slyke technique.

1. *Analysis of Dissolved Gases.* (For a complete account of these methods, the reader should refer to the text cited, pp. 269–442.)—The blood or other solution to be examined is taken into an extraction chamber over mercury, together with a suitable reagent, and outgassed by shaking under reduced pressure (the vapor pressure of the particular mixture present plus the pressure of the released gas at a volume of approximately 50 cc). The extraction chamber is calibrated at three fixed points, and the pressure (p_1) exerted by the liberated gas is measured by an attached manometer at one of these three constant volumes, after adjusting the meniscus of the solution to the etched mark defining the desired volume. A measured amount of gas-free reagent is then introduced, and when this has absorbed the desired component of the extracted gas mixture, the meniscus of the solution is adjusted to the same reference mark as before and the diminished pressure (p_2) read on the manometer. The difference, p_1-p_2, minus a correction $\boldsymbol{c}$, gives the pressure exerted by the gas removed by the reagent and affords the basis for calculating the amount of this gas in the measured sample of blood or other solution which was investigated. The significance of the ***c correction*** will be discussed in a moment.

2. *Analysis of Gas Mixtures.* (For a complete account of these methods, refer to the text cited, pages 106–160.)—The fixed volume at which the analysis is to be made is selected with reference to the amount of gas sample at hand. A pressure (p_o) is determined when the mercury meniscus is adjusted to the desired reference mark, and the extraction chamber contains no gas, but with the walls moistened by a film of gas-free water. The gas sample is introduced and the pressure (p_1) which it exerts is measured with the mercury again adjusted to the same reference mark. The pressure exerted by the sample is then calculated as $p_s=p_1-p_o$. A measured amount of reagent is admitted to remove one component of the gas mixture. When reaction is complete, the pressure (p_2) exerted by the residual gas is measured with the mercury meniscus again adjusted to the reference mark. The pressure exerted by the absorbed component is calculated as $p_s-K[p_2-(p_o+\boldsymbol{c})]$, where K is a factor to correct for the change in the fixed volume resulting from the addition of a known amount of reagent, and $\boldsymbol{c}$ is a correction similar to the one mentioned in the preceding paragraph.

III. SIGNIFICANCE OF THE VAN SLYKE *C CORRECTION*

Van Slyke explains the ***c correction*** for the two types of analyses as follows. Referring to the analysis of blood or dissolved gases, he states (p. 279):

"From the p_1-p_2 value observed it is usually necessary, for precise results, to deduct a correction which in the calculation formulae used is indicated by **c**.

The ***c correction*** is obtained by performing a blank analysis, in a manner directed for each type of determination. The p_1-p_2 value found in the blank constitutes the ***c correction.*** The ***c correction*** may be the sum of two components. One of them is a slight amount of gas which may be yielded by the reagents themselves. The other component is the fall in the manometer reading caused, even when no gas is removed, by the introduction of a given volume of absorbent solution. The introduction of solution between the two manometer readings p_1 and p_2 lowers the p_2 value merely by increasing the volume of liquid between the mercury surface and the water meniscus [1] at the moment of reading. Thereby the level of the mercury surface in the chamber, and, hence, also in the manometer, is lowered. The extent of this effect can be determined by means of blank analyses, in which, with the same amount of reagents but no gas in the chamber, the usual amount of absorbent solution is admitted. The manometer is read, with the water meniscus[2] in the chamber at the same mark before and after the admission of the absorbent solution. The difference between the two readings measures this component of the ***c correction.***"

It is also pointed out that the shape of the chamber will influence the value of this correction, which must accordingly be determined for each apparatus.

The ***c correction*** applied to methods for the analysis of gas mixtures is of the same nature, but since the mercury meniscus rather than that of the solution is always adjusted to the reference mark, the correction is of opposite sign. Concerning this type of analysis, Van Slyke states (p. 116):

"After the CO_2 has been absorbed"— (Author's note: this is, of course, the first component of respired air to be removed)— " the pressure exerted by the residual O_2+N_2 at 49 cc volume would be inexactly calculated as p_2-p_o. The zero manometer reading without any gas present is, on account of the 1 cc of NaOH solution present, slightly higher than the p_o observed at the beginning of the analysis with neither gas nor solution in the chamber. The weight of the short column of water in the chamber presses on the mercury there and in consequence raises the height of the mercury column in the manometer tube required to hold the meniscus in the chamber at the 50 cc mark. The ***c correction*** required for this effect varies somewhat with the shape of the bottom of the chamber and the consequent height of the column of 1 cc of solution. The correction is determined as follows: The p_o is determined, with the chamber free of both gas and visible amounts of water, as described on page 107. Then 1 cc of 1 *N* sodium hydroxide is admitted as described for absorption of CO_2, the chamber is evacuated till the mercury falls to the 50 cc mark, and the air is extracted from the solution by shaking the latter 1 minute. The extracted bubble of gas is ejected from the top of the chamber without loss of solution, as described on page 279. The chamber is again evacuated and the mercury meniscus is brought to the 50 cc mark. The manometer is again read. The difference between the two readings is the ***c correction.*** To determine ***c*** within 0.1 mm, one makes several check readings of p_o, and also several of p_o+c with the 1 cc of solution in the chamber. Once determined, the ***c correction*** serves for all analyses in which the same chamber is used."

This quotation is particularly significant to the present discussion, since the technique as prescribed by Van Slyke was followed in obtaining the data to be presented.

Van Slyke states that the ***c correction*** (as defined for the two types of analysis in the above quotations) is made up of one or both of two components. These he defines as follows: (p. 116), (1) "The weight of the short column of water [3] in the chamber pressing on the mercury there", or (p. 280), (1a) "the fall of the mercury surface in the chamber when absorbent solution is added." Case (1) applies to gas analysis, when the mercury meniscus is adjusted to the reference mark and the solution is above the mercury; case (1a) applies to the analysis of

[1] The term "water meniscus" should really be designated "solution meniscus", since the liquid is actually a water solution of various substances, and its saturation pressure is not exactly that of pure water.
[2] See footnote 1.
[3] See footnote 1.

dissolved gases when the solution meniscus is adjusted to the reference mark. The second component is (p. 279), (2) "A slight amount of gas which may be yielded by the reagents themselves."

In addition to the two components mentioned by Van Slyke, there is a third component which contributes to the total difference in pressure represented by this ***c correction.*** This is the lowering of vapor pressure with the introduction of the absorbing solution. The present discussion is directly concerned with this vapor pressure lowering.

The true nature and effect of the ***c correction*** can be shown by following through the procedure for the determination of CO_2 in respired air. In the following, p (with appropriate subscripts) will be used to identify the manometer pressures noted in Van Slyke's test (actual pressures—not merely readings of one arm of the manometer), and P (with subscripts) to identify the actual gas pressures or saturated vapor pressures. The subscript H_2O designates saturated water vapor, and the subscripts CO_2, O_2, and N_2 designate pressures exerted by these gases. The subscript H_2O' designates the saturation pressure of water over the normal sodium hydroxide solution (after reaction with CO_2). The height and density of the normal sodium hydroxide are expressed as h and d, respectively. The volumes at which pressures are measured before and after the introduction of the hydroxide are designated as V_1 and V_2, respectively. (It is assumed that temperature is constant, and that equilibrium is always attained.)

A pressure p_0 is measured at V_1 when the extraction chamber contains saturated water vapor, but with no gas or water over the mercury. Hence,

$$p_0 = P_{H_2O}. \tag{1}$$

The respired air is admitted and a pressure p_1 measured at V_1. It follows that

$$p_1 = P_{H_2O} + P_{CO_2} + P_{O_2+N_2}. \tag{2}$$

The pressure exerted by the sample (P_s) at V_1 is correctly given by

$$p_1 - p_0 = P_s = P_{CO_2} + P_{O_2+N_2}. \tag{3}$$

The hydroxide solution is admitted and CO_2 is removed. The residual pressure p_2, measured at V_2, is

$$p_2 = P_{H_2O'} + \frac{hd}{13.6} + (P_{O_2+N_2})_{V_2}. \tag{4}$$

Since

$$(P_{O_2+N_2})_{V_2} = \frac{V_1}{V_2}(P_{O_2+N_2})_{V_1} \tag{5}$$

$$p_2 = P_{H_2O'} + \frac{hd}{13.6} + \frac{V_1}{V_2}(P_{O_2+N_2}). \tag{6}$$

Subtracting (6) from (2):

$$p_1 - p_2 = P_{H_2O} - P_{H_2O'} - \frac{hd}{13.6} + P_{CO_2} + P_{O_2+N_2} - \frac{V^1}{V_2}(P_{O_2+N_2}). \tag{7}$$

Solving for P_{CO_2} in (7):

$$P_{CO_2} = P_{H_2O'} - P_{H_2O} + \frac{hd}{13.6} - P_{O_2+N_2}\left(1 - \frac{V_1}{V_2}\right) + p_1 - p_2. \tag{8}$$

Solving for $P_{O_2+N_2}$ from (6):

$$P_{O_2+N_2} = \frac{V_2}{V_1}\left(p_2 - P_{H_2O'} - \frac{hd}{13.6}\right). \tag{9}$$

Substituting this value in (8):

$$P_{CO_2} = p_1 - P_{H_2O} - \frac{V_2}{V_1}\left(p_2 - P_{H_2O'} - \frac{hd}{13.6}\right). \tag{10}$$

The equation given by Van Slyke (for the computation of P_{CO_2}) is

$$P_{CO_2} = P_S - P_{O_2+N_2} \tag{11}$$

or

$$P_{CO_2} = p_1 - p_0 - \frac{V_2}{V_1}[p_2 - (p_0 + c)]. \tag{12}$$

Substituting P_{H_2O} for p_0 from (1):

$$P_{CO_2} = p_1 - P_{H_2O} - \frac{V_2}{V_1}(p_2 - P_{H_2O} - c). \tag{13}$$

If P_{CO_2} is correctly given by both (10) and (13), then

$$c = \frac{hd}{13.6} - (P_{H_2O} - P_{H_2O'}). \tag{14}$$

The first term on the right-hand side of (14) represents the hydrostatic head, and the second term represents the vapor pressure lowering. Since, in the present work, the influence of any dissolved gas upon c was eliminated by using gas-free water and solutions, a term for the effect of such dissolved gas was not included in the equation.

In an analogous derivation of c for the case of blood gas analysis, which is not complicated by the factor expressing change in volume (since the meniscus of the solution is always adjusted to one fixed reference mark), one obtains the expression

$$c = \frac{hd}{13.6} + (P_{H_2O} - P_{H_2O'}). \tag{15}$$

where P_{H_2O} and $P_{H_2O'}$ really represent the vapor pressures of the liquid (e. g., blood) from which gas was extracted, and of the mixture of this liquid with the absorbing reagent, respectively. If the reagents were not gas free, a term should be added to equation (15) which would take this into account.

It is of course a fundamental requirement of such gasometric methods that all quantities of gas which are directly compared during an analysis be reduced to the same condition of temperature, pressure (or volume), and humidity. Van Slyke undoubtedly had this in mind, and made no mention of a vapor pressure lowering (in connection with the determination of ***c corrections***) evidently because he considered this to be negligible. He does mention the possibility of error from such a source in connection with the use of a 5 N sodium hydroxide solution for the determination of carbon dioxide in whole blood, under circumstance which do not permit dilution of the reagent with the 0.1 N lactic acid solution already present (p. 285 of his text). The same sort of error is cleverly dodged in his technique for air analysis (p. 115), which prescribes the determination of oxygen, after absorption with a 4 N solution of potassium hydroxide containing sodium thiosulphate, by measurement of the residual nitrogen rather than by direct measurement of the oxygen. Thus the residual nitrogen is represented by the difference in pressure readings after the absorption of the oxygen, and after ejection of the residual nitrogen but retaining the reagent used to absorb oxygen. The oxygen is then obtained by difference. The reason for this step was not given, probably since it was thought to be obvious enough. However, this very point has been overlooked in at least one case which recently came to our attention, wherein the analyst was erroneously determining oxygen directly.

The determination of carbon dioxide, however, does not depend upon such a procedure to eliminate this error. Instead, reliance is

evidently placed upon the fact that the vapor pressure of a solution of 1*N* sodium hydroxide will not greatly differ from that of water. This is reasonably true, except for the fact that the lowering of vapor pressure (with addition of normal sodium hydroxide solution) increases with temperature so that the saturation-pressure curves for water and the hydroxide solution diverge appreciably at temperatures much above 20 C. It consequently follows that the determination of the actual value of ***c*** is dependent upon temperature, and the ***c correction*** determined at one temperature is not necessarily satisfactory for other temperatures. Thus the determination of the ***c correction*** of a particular apparatus once for all, as suggested, may not be adequate. The data to be presented will illustrate this point.

In addition to the above, the vapor pressure lowering as a function of temperature becomes larger in cases where the specified 4 *N* and 5 *N* reagents are used in the analyses of dissolved gases. Thus a ***c correction*** obtained when these reagents are used may be subject to error with change of temperature unless the reagents are successfully diluted with solutions already present in the extraction chamber. When any gas is in the extraction chamber, it may not be possible to dilute the stronger alkaline solutions satisfactorily, since they are admitted from the top of the chamber, where a small amount just under the inlet stopcock may exert an appreciable effect on the vapor pressure of the system.

IV. METHOD FOR DETERMINING THE EFFECT OF TEMPERATURE ON *C CORRECTIONS*

The effect of temperature on the value of this correction can be shown experimentally by repeating the technique prescribed by Van Slyke (already noted) over the range of temperature which may be expected in the ordinary laboratory. The temperature of this laboratory varies from about 20 to 31 C. This condition may appear extreme to those located in more desirable climatic surroundings, but it is not strange to anyone who has occupied a laboratory in Washington. This range of temperature was accordingly selected as significant.

The data were obtained for the following solutions, which are reagents used by Van Slyke.

1 *N* sodium hydroxide.

4 *N* potassium hydroxide containing 15 g of sodium thiosulphate per 50 cc (filtered and protected from air).

5 *N* sodium hydroxide.

In every case the solution was thoroughly shaken in the extraction chamber.[4] In addition, this procedure was repeated a number of times during the course of a series of observations in order to insure the maintenance of this condition, and check readings were taken thereafter. The pressures reported represent the average of at least three readings agreeing within 0.1 mm.

The mercury meniscus was adjusted to the reference mark in all cases. The height of the solution above the mercury was measured by means of a cathetometer, the density of the solution determined, and the hydrostatic pressure of the solution calculated therefrom in

[4] This procedure is supposed to remove all measurable amounts of dissolved gas.

order to establish the contribution of this factor to the total change in pressure or ***c correction.*** In addition, pressures were determined in the case of the 1 *N* sodium hydroxide both with solution present and expelled, so that the latter series of observations gave a direct reading of the vapor pressures of this solution without the added effect of the hydrostatic head of the solution.

Observations were made with the mercury meniscus adjusted to both the 50 cc and 2 cc marks. These two series represent the conditions existing during macro- and micro-analyses, respectively. The 0.5 cc mark was not used, since the mercury meniscus, rather than the meniscus of the solution, was adjusted to the reference mark and 1 cc of solution was over the mercury.

All measurements of pressure were made under conditions such that the temperature of the water in the jacket surrounding the extraction chamber and that of the room were equal (within 0.1° C) and so maintained over considerable periods (1 hour or more). It was found that no reliable results could be obtained unless such a temperature equilibrium was established, even though the temperatures of room and jacket were brought to the same value by the method suggested by Van Slyke. Data to illustrate this point and the possible errors involved will be given.

The pressures reported are in mm of mercury (and are not merely readings of one arm of the manometer). The zero of the manometer scale was obtained for both of the reference marks used, by means of the cathetometer.

The data obtained are presented in the form of curves where observed pressures are plotted against corresponding temperatures. These are in effect vapor-pressure curves, with an added component in some cases which results from the effect of the hydrostatic head of the solution. The curves are designated as follows:

Those marked *V* 50 refer to pressure readings taken with the mercury meniscus adjusted to the 50 cc mark, and those marked *V* 2 are corresponding pressures taken with the mercury adjusted to the 2 cc mark.

Curves marked P_{H_2O} represent pressures observed with no gas present in the chamber and with a film of gas-free water moistening the walls, but with no visible water. These curves are accordingly the vapor pressure curves of pure water, and are shown to be in agreement with known data.

Curves designated as P_{1N} represent pressures taken with no gas in the extraction chamber and with the walls moistened by a 1 *N* solution of sodium hydroxide, with no visible amount of solution. The curves marked P_{1N+S} represent pressures observed under the same conditions, but with a measured volume (1 cc) of solution over the mercury. The latter curves include the effect of hydrostatic pressure.

Curves designated as P_{4N+S} represent pressures noted with no gas in the extraction chamber, but with 1 cc of the 4 *N* potassium hydroxide solution containing sodium thiosulphate (according to previously noted formula) present. Those marked P_{5N+S} indicate pressures observed under the same conditions with a 5 *N* solution of sodium hydroxide.

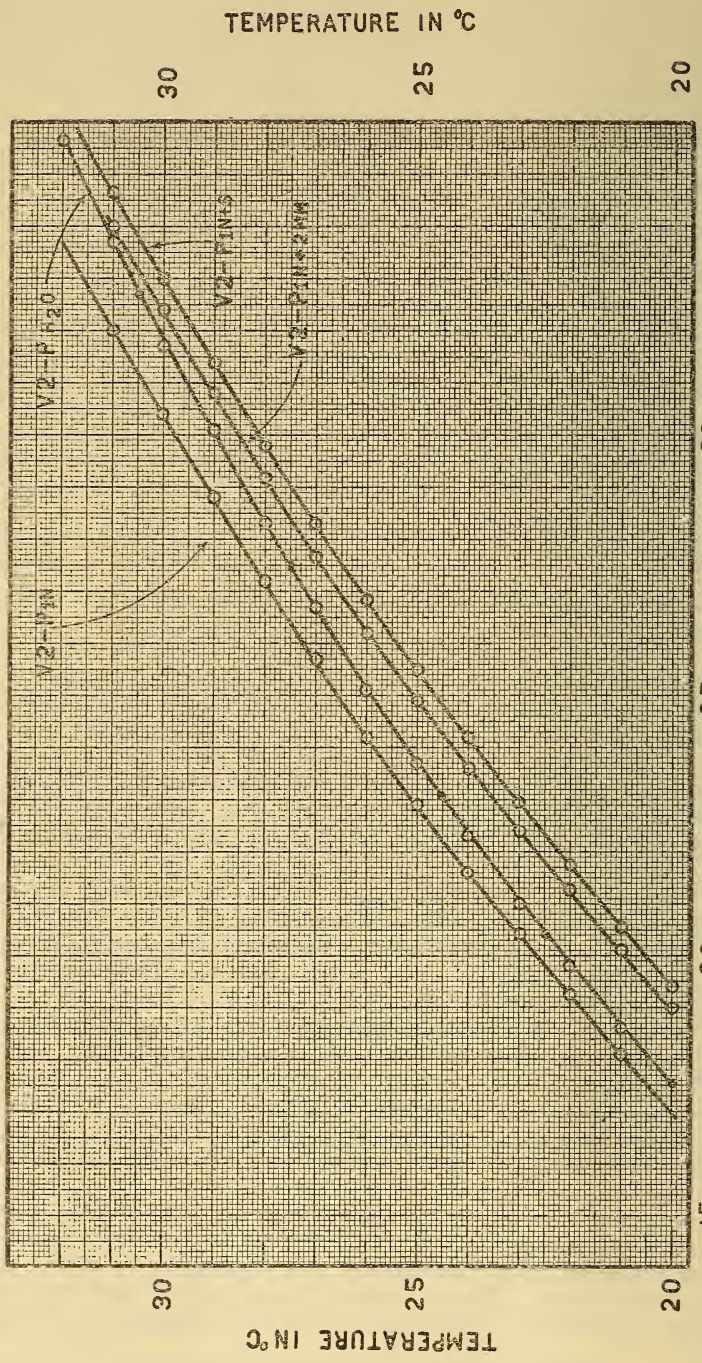

FIGURE 1.—*Vapor pressure data for water and pressures observed with the 1 N sodium hydroxide solution at the 2 cc volume.*

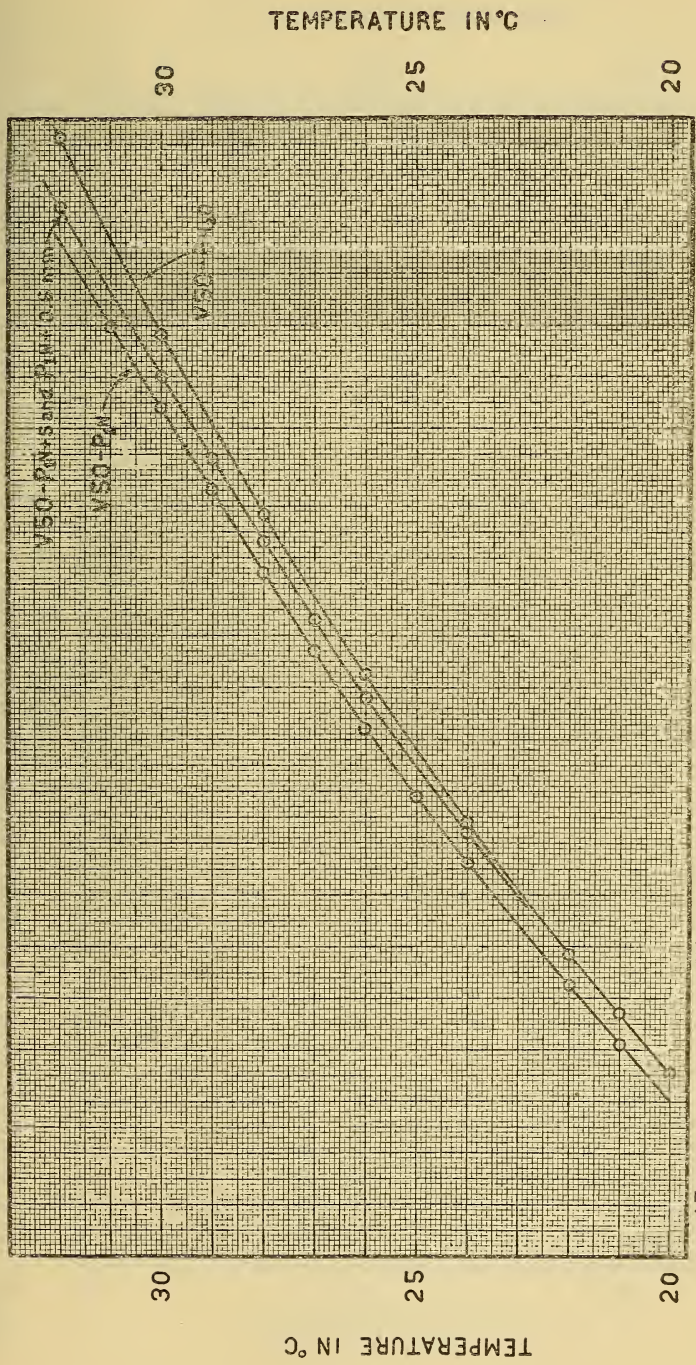

FIGURE 2.—*Vapor pressure data for water and pressures observed with the 1 N sodium hydroxide solution at the 50 cc volume.*

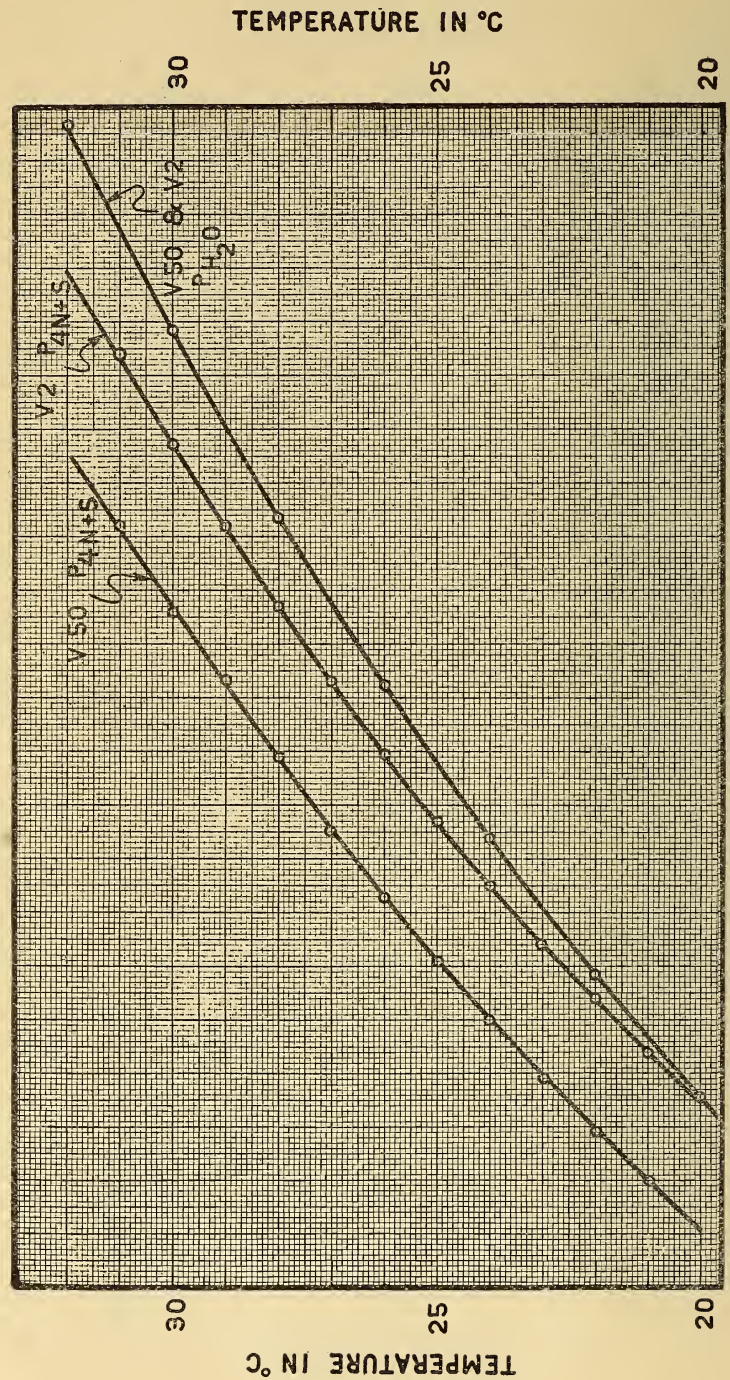

FIGURE 3.—*Vapor pressure data for water and pressures observed with the 4 N pot assium hydroxide+sodium thiosulphate solution at 2 cc and 50 cc volumes.*

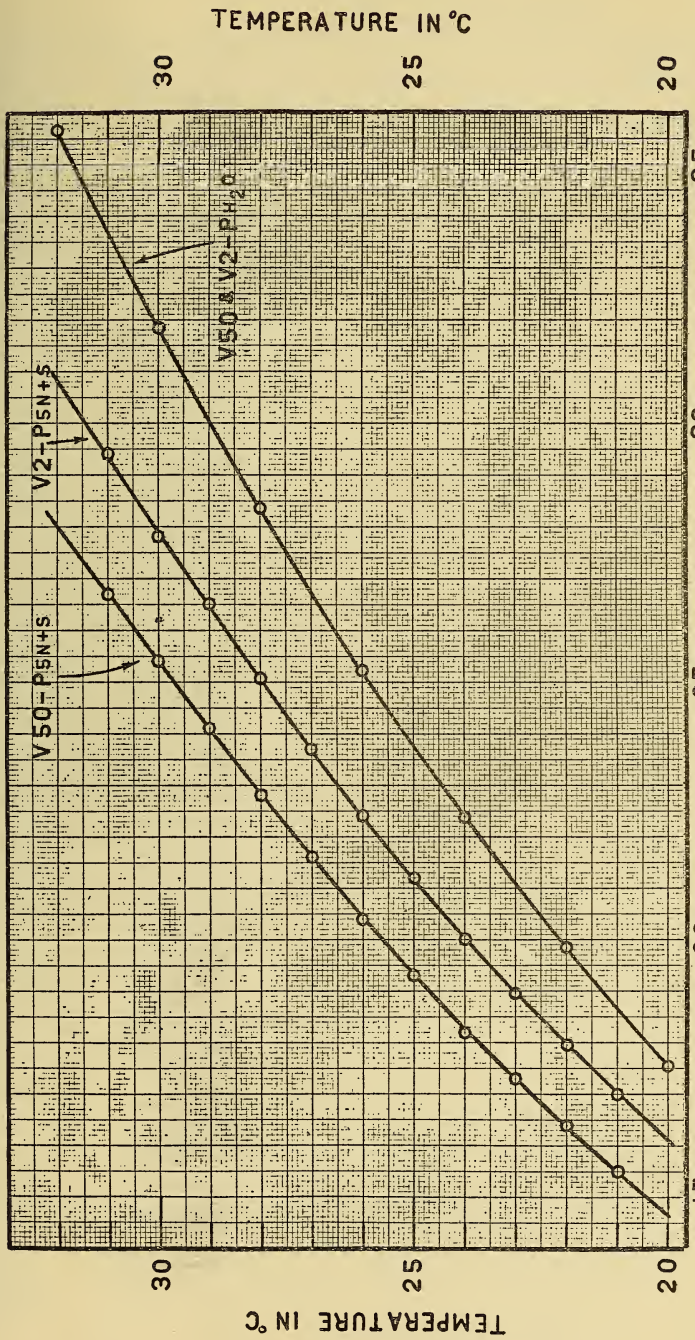

FIGURE 4.—*Vapor pressure data for water and pressures observed with the 5 N sodium hydroxide solution at 2 cc and 50 cc volumes.*

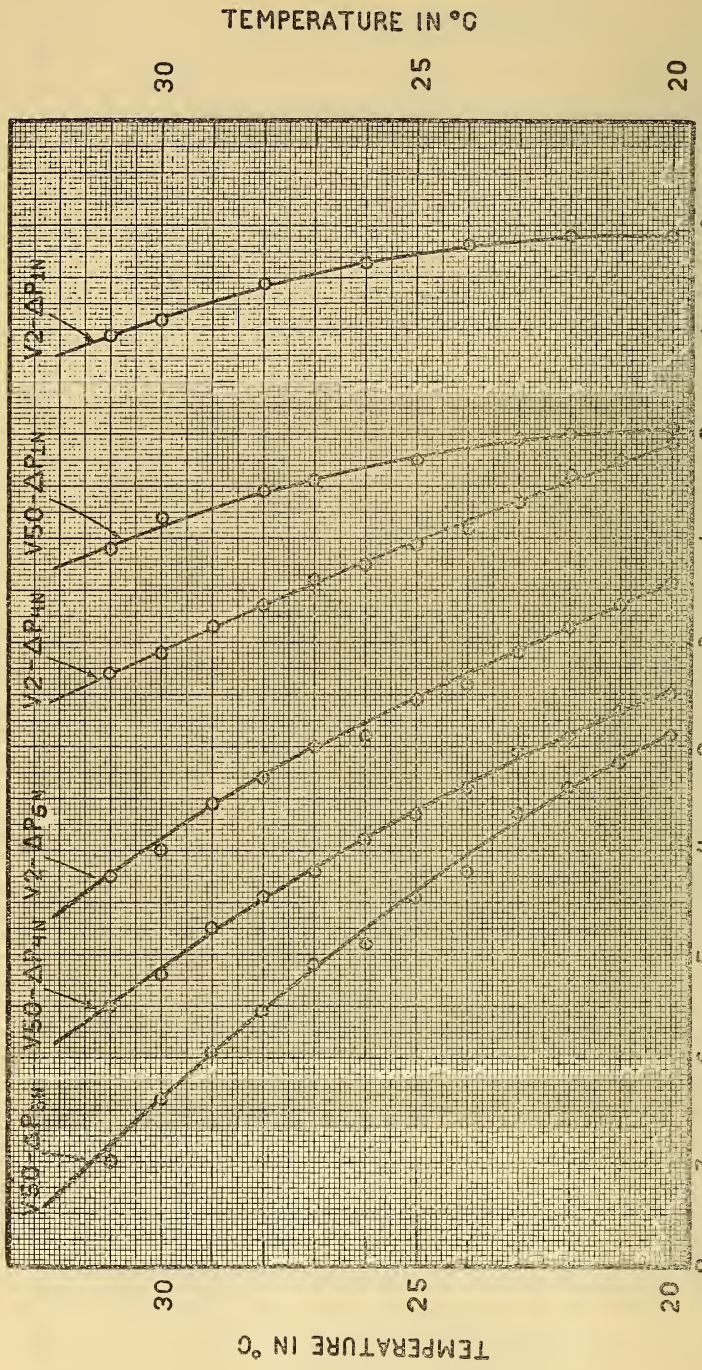

FIGURE 5.—*Values of the* **c** *correction at various temperatures.*

Curves for 1 *N* solution represent actual **c** *corrections* as applied to the analysis of gases (e.g., respired air).
Curves for the 4 *N* and 5 *N* solutions do not represent actual **c** *corrections* for the analysis of dissolved gases, but indicate the maximum errors which might occur if these solutions are not successfully diluted by the prescribed techinques.

V. DATA OBTAINED WITH THE 1 *N* SODIUM HYDROXIDE SOLUTION

This reagent is used to remove carbon dioxide, both in the analysis of gas mixtures, and from gases extracted from blood and other liquids. In the former case, the gas sample is measured when saturated with water vapor, while the residual gas remaining after absorption of carbon dioxide is measured at the saturation pressure of the reagent. The lowering of vapor pressure which occurs with the introduction of the reagent is small, but significant. The ***c correction,*** taken for the purpose of correcting for the hydrostatic head of reagent, will also correct for this lowering of vapor pressure at the particular temperature existing within the system at the time the ***c correction*** was measured. It will not correct for this lowering of vapor pressure for any other temperature at which the apparatus may be used in subsequent analyses. Whether or not the resulting error attains significance will depend upon the degree of divergence of the curve representing the vapor pressure of pure water from that representing the vapor pressure of the reagent, or from the vapor pressure of the reagent plus its hydrostatic pressure. The latter divergence represents the Van Slyke ***c correction.***

Data obtained for normal sodium hydroxide are given in figures 1 and 2, where the temperatures existing are plotted against the corresponding pressures. The curves of figure 1 represent the data for the volume 2 cc, and those of figure 2 for the volume 50 cc.

Referring to figure 1, the curve marked $V2-P_{H_2O}$ is the vapor pressure curve for pure water, and represents the p_o pressures of Van Slyke. The open circles represent values obtained experimentally with the apparatus employed, and the closed circles correspond to values given in International Critical Tables. The experimental values agree with the accepted data. The curve marked $V2-P_{1N}$ represents the experimental values obtained for the vapor pressures of the 1 *N* sodium hydroxide reagent. The divergence of these two curves is immediately noted.

The two sets of data just mentioned should not depend upon the fixed volume selected for the measurement, since no gas or visible amount of reagent is present. With 1 cc of reagent above the mercury, the values obtained will differ for the 2 cc and 50 cc fixed volumes, since the hydrostatic pressures are not equal at the two reference points. The curve marked $V2-P_{1N+s}$ represents values for the blank analyses when the 2 cc volume is chosen. It will be noted that at 20 C the value of P_{1N+s} is 19.4 mm, and the vapor pressure of water (P_{H_2O}, or p_o of Van Slyke) is 17.5+mm, a difference of 1.9 mm; but at 31 C, the value of P_{1N+s} is 34.7, and the vapor pressure of water is 33.7 mm, a difference of 1.0 mm. Thus if the ***c correction*** was obtained for the apparatus once for all at one of these temperatures, and analyses were subsequently conducted at the other temperature, the ***c correction*** would be in error by about 1 mm. The percentage error involved would depend upon the initial pressure exerted by the sample. This is usually about 500 mm, making the error about 0.2 percent. The accuracy claimed for the method is 0.05 percent (see page 113 of text), or, in case of the isolation method of Van Slyke, Sendroy and Liu (see p. 119), it is thought an accuracy of 0.0001 percent is attained. Under these circumstances, 0.2 percent becomes

significant. The case selected is, of course, extreme. If the analyst were fortunate enough to have obtained a ***c correction*** at say 25 C and performed an analysis at 26 C, the error would be about one tenth of the former one under like conditions. It should, however, be remembered that a lower initial pressure exerted by the sample will increase the error.

Referring again to figure 1, the curve $V2-P_{1N+2mm}$ is of interest. This represents the values for the vapor pressures of the 1 N solution (curve $V2-P_{1N}$) corrected for the hydrostatic pressure of the solution. The latter value was obtained by measuring the height and density of the solution and converting to mm of mercury. It will be seen that these values are slightly lower than those obtained by measuring the pressures with the solution over the mercury, although the two curves are nearly parallel. The difference is of the right order of magnitude to be explained by differences of capillarity. Corrections for capillarity are large in a tube of 4 mm diameter (which is the case at the 2 cc interval). It is worthy of note that the ***c correction*** obtained for 30 C was 1.1 mm, whereas the measured hydrostatic head of the solution was 2 mm.

Figure 2 illustrates corresponding data for the 1 N solution when the 50 cc fixed volume was chosen. In this case the hydrostatic pressure of the solution as measured was only 0.6 mm, and the values for the vapor pressures of the 1 N solution corrected for this figure lie along the curve of the observed values for the pressure P_{1N+s}. The differences between the P_{H_2O} and P_{1N+s} values are negligible at the lower temperatures, but the two curves diverge to give a ***c correction*** of 1 mm at 31 C, so that the error involved in assuming ***c*** independent of temperature is of the same order of magnitude as the one discussed for the $V2$ values.

VI. DATA OBTAINED WITH THE 4 *N* POTASSIUM HYDROXIDE SOLUTION CONTAINING SODIUM THIOSULPHATE, AND THE 5 *N* SODIUM HYDROXIDE SOLUTION

These data are illustrated graphically in figures 3 and 4 and are given for both the 2 and 50 cc fixed volumes. It is at once noted that any solution approaching such concentrations in the extraction chamber would cause large errors if ***c*** is assumed to be independent of temperature. For example, in the case of the 5 N solution at the 50 cc volume, ***c*** is about -2.9 mm at 20 C and about -6.9 mm at 31 C. The difference of 4 mm over an initial pressure of 400 mm represents an error of 1 percent, which is certainly too great to fit into this scheme of analysis. Such errors are probably never encountered in actual practice if the prescribed techniques are closely followed. The actual magnitude of the errors which do occur will depend upon the extent to which the reagent is successfully diluted with other solutions which may already be in the extraction chamber, and the complete removal of all traces of the reagent from under the upper stopcock of the extraction chamber. It must also be remembered that ***c***, while always the same general type of correction, is itself different for the many procedures described by Van Slyke. The determination of each constituent, in each type of analysis of dissolved gases, may have a different ***c***.

VII. CHANGE OF *C CORRECTIONS* WITH TEMPERATURE

Figure 5 represents graphically the differences observed between the P_{H_2O} values and those for the three reagents when 1 cc of the solution was above the mercury. These are the ***c corrections*** for the 2 cc and 50 cc volumes, and are plotted against temperature. If the ***c correction*** is obtained at one temperature and applied thereafter at any other temperature, the percentage error is determined by reading the value of ***c*** at the second temperature, subtracting from the first value obtained, and dividing this difference by the initial pressure exerted by the gas sample.

It should be remembered that the ***c corrections*** as derived do not include the component designated by Van Slyke as the small amount of gas which may be yielded by the reagents themselves. This is true since all the reagents employed were gas-free. Considering this component of the ***c correction,*** the value of the whole correction as usually applied may become doubtful if blanks are not performed with each analysis, since the reagents may be expected to hold varying amounts of gas in solution under different conditions of temperature and pressure, and these amounts, though small, exert decided effects on the pressures in small volumes.

VIII. EFFECT OF A DIFFERENCE OF TEMPERATURE BETWEEN THE WATER JACKET AND THE ROOM, AND THE ERROR WHICH MAY RESULT

The upper stopcock of the Van Slyke apparatus and a very small portion of the extraction chamber connected thereto extend above the water jacket. Liquid located on the walls of this portion of the apparatus exerts a decided effect on the resultant vapor pressure of the entire system. The tendency is, of course, for the resultant saturation pressure to be very nearly that of the solution at its coldest point. The following experiment illustrates this. The walls of the extraction chamber were moistened with gas–free water, with no visible amount of water. The room and the water in the jacket were held at 20.2 C. The observed pressure at 2 or 50 cc was 17.8 mm, which checks the value for the saturation pressure of water at that temperature. The jacket was then surrounded with a warm towel until the thermometer within the jacket registered 22.6 C. The room temperature, recorded at the same level (about 1 foot distant) was now observed to be 20.5 C. The pressure under these conditions was 18.4 mm, which is closer to the vapor pressure of water at 20.5 C (18.1 mm) than at 22.6 C (20.6 mm). The jacket was allowed to cool to the laboratory temperature. Readings taken were: Room, 20.2 C; jacket, 22.0 C; p, 17.9 mm; (P_{H_2O} = 17.8 mm at 20.2 C). Room, 20.2 C; jacket, 21.0 C; p, 17.8 mm; (P_{H_2O} = 17.8 mm at 20.2 C). Room, 20.1 C; jacket, 20.6 C; p, 17.8 mm; (P_{H_2O} = 17.7 mm at 20.1 C). In every case the significant temperature, based upon the observed vapor pressure, was that of the room rather than the jacket. When the room was heated, observations were made as follows: Room 23.5 C; jacket 23.1 C; p, 21.2 mm; (P_{H_2O} = 21.2 mm at 23.1 C).

It is consequently very important that the jacket temperature and laboratory temperature be closely equal, rather than no further apart

than 1° C, as specified (see p. 278 of text). Furthermore, the glass parts of the apparatus protruding from the jacket should be in temperature equilibrium with the room. Otherwise, an error will be made in correcting the pressure exerted by the gas sample for any change in the vapor pressure of water. Thus in the above case, when the jacket temperature was read as 21.0 C and the vapor pressure corresponded to a temperature of 20.2 C, an error of 0.9 mm would have been made when the correction was applied for the vapor pressure of water, and this in a case where the temperatures of room and jacket differed by only 0.8° C. At higher temperatures the error increases, so that a difference of 1° C at 30 to 31 C might involve an error of 1.9 mm, or nearly one half of 1 percent if the pressure exerted by the original sample had been 400 mm.

IX. CONCLUSION

Two suggestions follow naturally after consideration of the data presented.

1. The Van Slyke ***c corrections*** may be determined over the entire range of laboratory temperatures, and the appropriate correction selected for the particular analysis on hand.

2. The Van Slyke apparatus may be modified by placing two parallel chambers in the water jacket, one to function as an extraction and reaction chamber, and the other as a fixed volume buret.

The latter procedure would possess several additional advantages. It would always be possible to avoid redissolving some portion of an extracted gas sample, for which the correction is troublesome and not always satisfactory. This could be achieved by transferring the liberated gas from the extraction chamber to the buret under the pressure at which the extraction occurred. Each reagent could be freed from gas in the apparatus before bringing the gas mixture into the reaction chamber. Physical solution of components of the gas mixture in the reagent could be reduced for macro-analyses and almost avoided for micro-analyses. The various fractions of the gas mixture would always be accurately measured under the same condition of humidity. The measurement of gas volumes (or pressures) would always be made by adjusting a clean mercury meniscus to a reference mark, thus avoiding obscure solution menisci. Solutions from which gas samples were extracted, as well as reagents subsequently employed, could be expelled from the extraction chamber at each step of the analysis. This technique would permit straightforward clean reactions with no interference, either chemical or physical, from accumulating mixtures of various liquids that have already served their purpose in the analysis. Reagents of any desired strength could be employed. There would be no hydrostatic pressures to correct for, and the ***c correction***, as well as all others applied by Van Slyke, would merely resolve into a simple correction for the change of pressure of the gas and saturated water vapor with any change of temperature which might occur during the analysis.

Washington, February 14, 1934.